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see attached report

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-86-K-0547

Physical and Chemical Characteristics of Organoboranes

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October 19, 1988

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Technical Reports and Journal Articles

Technical Reports

1. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes
   N. N. Joshi, M. Srebnik and H. C. Brown

2. A Comparative Study of Dialkylboron Chlorides and Triflates for the Enolization of Ketones. The Controlled Stereospecific Synthesis of Either [*E*]- or [*Z*]-Enol Borinates
   H. C. Brown, B. Singaram, R. K. Dhar, P. K. Pandiarajan and R. K. Dhar

3. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes
   N. N. Joshi, M. Srebnik and H. C. Brown
   Oral presentation at the 146th Meeting of the American Chemical Society in Los Angeles, CA, September 25-30, 1988

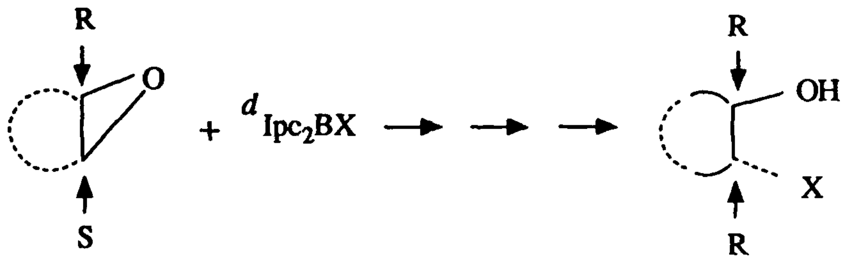
Journal Articles

1. Enantioselective Ring-Cleavage of *meso*-Epoxides with B-Halodiisopinocampheylboranes
   N. N. Joshi, M. Srebnik and H. C. Brown
   J. Am. Chem. Soc. **1988**, *110*, 6246

Summary of Accomplishments

1. Enantioselective Ring Cleavage

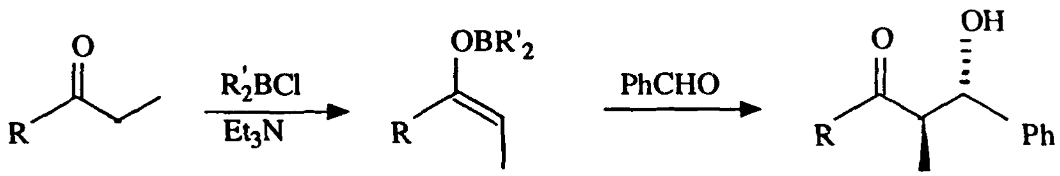
This subject has been detailed in Technical Reports (1), April 26, 1988, and (3), May 18, 1988. We have succeeded in obtaining optically active 1,2-halohydrins from *meso*-epoxides and chiral organoboranes. This is the first time such an asymmetric transformation has been accomplished. epoxides.



52 - ~ 100% ee for
X = Br, I

2. Enol Borinates

This topic was the subject of Technical Report (2), May 13, 1988. In essence we have found conditions for obtaining [*E*]-enol borinates from ketones and readily available dialkylchloroboranes.



[*E*]-borinate ~ 80-99%

anti-Aldol 80-99%

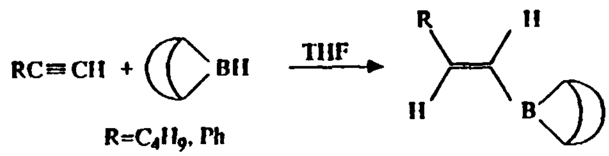
Reaction of the [*E*]-enol borinate with an aldehyde then gives the *anti*-aldol product. This methodology therefore complements the known process of obtaining [Z]-enol borinates from ketones and dialkyl boron triflates, which in turn provide *syn*-aldol products.

3. Hydroboration of Alkenes

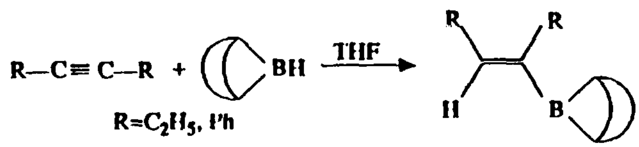
This project was only briefly covered in the End-of-the-Year Reports (July 21, 1987 and July 22, 1988) and therefore will now be presented in greater detail.

Monohydroboration of symmetrically substituted internal alkynes, such as 3-hexyne and diphenylacetylene, with an equivalent of 9-BBN can be carried out at 0°C and 25°C respectively, producing the B–vinyl derivatives in 95-98% yields. The dihydroboration of 3-hexyne (0.25 *M*) with 2 equiv of 9-BBN (0.5 *M*) can only produce 56% of *gem*-dibora derivatives with 44% of B–vinyl derivatives at 25°C. However, the formation of *gem*-dibora derivatives can be improved by increasing the temperature (65°C) and concentration (0.75 *M*). The reaction of diphenylacetylene with 2 equiv of 9-BBN can only produce B-vinyl derivatives at 25°C, with no dihydroborated product. The dihydroboration of terminal alkynes, such as 1-hexyne and phenylacetylene, with 2 equiv of 9-BBN can produce *gem*-dibora derivatives in 81-90% yields. But the monohydroboration of 1-hexyne and phenylacetylene with an equivalent of 9-BBN can only provide a mixture of B-vinyl and *gem*-dibora derivatives in 64:36 and 76:24 respectively. Fortunately, the monohydroboration of 1-hexyne with 9-BBN can be improved by use of 100% of excess of terminal alkyne, making possible the preparation of the corresponding B-[*E*]-1-hexenyl-9-BBN in 85% yield with no dihydroborated product. But in the case of phenylacetylene, the monohydroboration can only be improved to 83:17 from 76:24.

No general synthesis of B-vinyl and dibora derivatives has been studied in detail using various hydroborating agents and alkynes. Consequently, a systematic study was undertaken to prepare various B-alkenyl and dibora derivatives from representative alkynes using 9-BBN (eqs 1-4).



(1)



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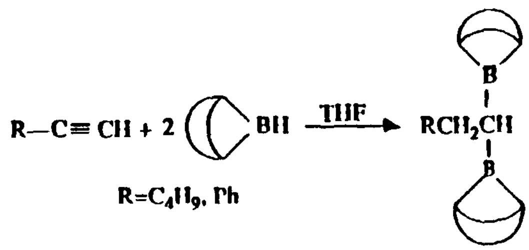

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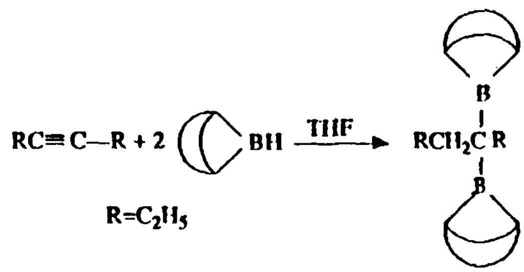

(4)

All yields were ≥ 80%. The products were confirmed by conversion to the corresponding aldehydes.